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Title: Osmium uptake, distribution and 187Os/188Os and 187Re/188Os composition in Phaephyceae macroalgae, Fucus vesiculosus: implications for determining the Os isotope composition of seawater

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Osmium uptake, distribution, and $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ compositions in Phaeophyceae macroalgae, *Fucus vesiculosus*: Implications for determining the $^{187}Os/^{188}Os$ composition of seawater

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Abstract

The osmium isotopic composition ($^{187}Os/^{188}Os$) of seawater reflects the balance of input from mantle-, continental- and anthropogenic-derived sources. This study utilizes the Phaeophyceae, *Fucus vesiculosus,* to analyse its Os abundance and uptake, as well as to assess if macroalgae records the Os isotope composition of the seawater in which it lives. The data demonstrates that Os is not located in one specific biological structure within macroalgae, but is found throughout the organism. Osmium uptake was measured by culturing *F. vesiculosus* non-fertile tips with different concentrations of Os with a known $^{187}Os/^{188}Os$ composition (~0.16), which is significantly different from the background isotopic composition of local seawater (~0.94). The Os abundance of cultured non-fertile tips show a positive correlation to the concentration of the Os doped seawater. Moreover, the $^{187}Os/^{188}Os$ composition of the seaweed equaled that of the culture medium, stongly confirming the possible use of macroalgae as a biological proxy for the Os isotopic composition of the seawater.

Keywords

Osmium, macroalgae, rhenium, isotope composition, seawater, *Fucus vesiculosus*

1. Introduction

Osmium (Os) is one of the least abundant elements in seawater, with a concentration in the open ocean of ~0.01 ppt (Chen and Sharma, 2009; Gannoun and Burton, 2014; Levasseur et al, 1998; Sharma et al, 1997), which is significantly lower than the average crustal abundance (30 - 50 ppt; Peucker-Ehrenbrink and Jahn, 2001; Wedepohl, 1995). Thermodynamic data predict that Os in seawater likely exists as the species OsO_4^0, $HOsO_5^-$ and $H_3OsO_6^-$ (Palmer et al., 1988; Yamashita et al., 2007), with all speciated forms present in the highest oxidation state available to Os. However, chloride complexing is also possible ($OsCl_6^-$, Cotton and Wilkinson, 1988), and it has also been suggested that Os exists as an organo-complex (Levasseur et al., 1998). Osmium in seawater has been shown to exhibit both conservative and non-conservative behaviour (Chen and Sharma, 2009; Gannoun and Burton, 2014), with the present day seawater Os isotope ($^{187}Os/^{188}Os$) composition inferred to reflect Earth surface processes, i.e. the balance of inputs from radiogenic continental-derived and unradiogenic mantle-derived sources (Peucker-Ehrenbrik and Ravizza, 2000; Cohen et al., 2003; Banner, 2004).

Brown macroalgae (i.e. seaweed) are known to concentrate many metal cations and metal oxoanions in a variety of complexes with biopolymers, e.g. alginate, proteins, polysaccharides of the cell wall, fucans, etc. (Davis et al., 2003). To date, positively charged metals associated with macroalgae have been extensively studied (e.g., Ragan et al., 1979; Chapman and Chapman, 1980; Karez et al., 1994; Lobban and Harrison, 1994; Raize et al., 2004). However, relatively little is known about the mechanisms by which macroalgae uptake negatively charged metal oxoanions. To our knowledge, there have been no studies discussing the uptake amount and accumulation of Os by any macroalgae species, although it is known that Os, in addition to Re can accummulate in

seaweed (Scadden et al, 1969; Yang, 1991; Mas et al., 2005; Prouty et al., 2014; Racionero-Gómez et al, 2016; Rooney et al, 2016). The brown macroalgae (Phaeophyceae) *Fucus vesiculosus* is observed to be one of the greatest accumulators of metals (Scadden et al, 1969; Morries and Bale, 1975; Bryan, 1983; Yang, 1991; Rainbow and Phillips, 1993; Karez et al., 1994; Mas et al., 2005; Racionero-Gómez et al., 2016).

As such, this study investigates *F. vesiculosus* to establish both the specific sites and the mechanisms of Os accumulation. We also evaluate the importance of macroalgae in recording the direct Os isotope composition of seawater. Here we present the Os abundance for different structures of *F. vesiculosus*: holdfast, stipe, tips, vesicles and blades (Fig. 1) and we determine the uptake rate of Os in macroalgae via cultures of *F. vesiculosus* under different Os concentrations. We also demonstrate experimentally that macroalgae records the Os isotope composition of the local environment in which it lives (i.e. seawater), indicating that seaweed has the ability to record the interaction between the ocean and the Earth's surface, a mechanism proposed for brown algae based on samples collected from the west coast of Greenland and the Gulf of Mexico (Rooney et al, 2016). In addition, we present the rhenium (Re) abundance, and the $^{187}Re/^{188}Os$ composition of the macroalgae studied.

2. Material and methods

2.1 Macroalgae used in this study: *Fucus vesiculosus*

F. vesiculosus is a common brown macroalgae found along sheltered shores of the North Sea, Baltic Sea, Atlantic Ocean and Pacific Ocean. *F. vesiculosus* produces air bladders annually allowing the individual fronds to float in the upper portion of the water column to permit photosynthesis. The species comprises an anchoring holdfast

and a frond made up of a stipe, blades, tips and vesicles (Fig. 1). The growth rate of *F. vesiculosus* ranges between 0.05–0.14 cm/day (Carlson, 1991; Strömgren, 1977), with the species having a life span between 3 to 5 years (White, 2008). The species is annually episodic, gonochoristic and highly fecund (i.e. prolific; White, 2008). *F. vesiculosus* has both fertile tips and non-fertile tips. Fertile tips contain receptacles from which the gametes are released to the seawater and the eggs are fertilized externally. The zygote then starts to develop as soon as it settles into a substrate (Graham and Wilcox, 2000). Non-fertile tips are composed of a parenchymatous thallus i.e. tissue like structure (Graham and Wilcox, 2000; Hiscock, 1991; White, 2008).

The *F. vesiculosus* samples were collected from within the harbour at Staithes and adjacent to the eastern (seaward) side of the east harbour wall, North Yorkshire, UK (Fig. 2) in May, 2014 and June, 2015 (Fig. 2). The Lower Pliensbachian Staithes Sandstone Formation (a 30m thick argillaceous silty sandstone interbedded with 2 to 4 m thick sequences of fine-grained laminated sandstone) comprises the geology of the harbour, beach and village of Staithes, with the cliffs to the east of the harbour coinsisting of the Upper Pliensbachian Cleveland Ironstone Formation (dark argillaceous siltstone and silty sandstone with oodial ironstone; Rawson and Wright, 2000). The May 2014 *F. vesiculosus* collection (Five *F. vesiculosus* specimens held on the same rock) were taken from the eastern side of the east harbour wall (54°33'32.5"N 00°47'15.5"W; Fig. 2). These *F. vesiculosus* samples were utilised to determine the Os abundance of specific structures of the macroalgae. Additional *F. vesiculosus* samples collected in June 2015 were taken from a single location to avoid genetic variation from the mouth of Staithes Beck within the harbour of Staithes (54°33'32.8"N 00°47'25.5"W; Fig. 2). The non-fertile tips (~100) of the June 2015 sample collection were utilised for culture experiments. Seawater used in the culture experiments was taken from the same

111 location as the June 2015 *F. vesiculosus* sample set. An aliquot of the collected seawater
112 was utilised for Re-Os abundance and isotope composition determination.
113
114 **2.2 Sample preparation and culturing**
115 Prior to analysis all collected specimens were kept individually in plastic sample
116 bags for transport, and stored in a freezer (-10 ºC) for 48 h. Each specimen was washed
117 and rinsed in deionised (Milli-Q™) water to remove any attached sediment and salt. To
118 establish the abundance and distribution of Os in the macroalgae the sample was
119 divided into different structural components: fertile tips, non-fertile tips, vesicles, stipe,
120 holdfast, and blades (Fig. 1). In addition, a mixture of the above components was
121 created to determine an average Os abundance of the whole macroalgae structure. Each
122 structure was dried in an oven at 60 ºC for 12 hrs, prior to powdering to a powder in an
123 agate pestle and a mortar.
124 In addition, to investigate the uptake of Os by macroalgae, culture experiments
125 were conducted in seawater (modified after Gustow et al. (2014)) in the School of
126 Biological and Biomedical Sciences at Durham University. In total, three separate
127 culture experiments were conducted, with each experiment replicated a total of three
128 times. For each experiment, non-reproductive apical thallus tips were taken from
129 separate *F. vesiculosus* June 2015 specimens of the geographical area (length ≥1.5 cm;
130 wet weight (WW) = 0.12–0.15 g) without visible microalgae (i.e. epiphytes). The apical
131 thallus tips were placed into a 250 mL glass jars containing two plastic mesh shelves.
132 Three tips were placed in the bottom of the jar and three tips were placed in each mesh,
133 having in total nine tips of different specimens in each jar (see Fig. 3). All culture
134 experiments were carried out using filtered (0.7 μm) seawater from Staithes, North
135 Yorkshire, UK (54°33'32.8"N 00°47'25.5"W; Fig. 2) collected in June 2015. The

seawater was collected and stored in cleaned PFA Teflon bottles (following the method of Sharma et al., 2012). The source of Os used to dope the natural seawater for the culture experiments is DROsS (Durham Romil Osmium Standard; Nowell et al., 2008). DROsS is an in-house Os solution reference material that possesses a $^{187}Os/^{188}Os$ composition of 0.160924 ± 04 (2SD; Nowell et al., 2008). The DROsS solution utilized in this study is in chloride form. The Re and Os abundance and isotope composition of the collected seawater at Staithes was also determined as part of this study (see methodology below).

To reduce evaporation while to allowing gaseous exchange with the atmosphere all the jars were loosely sealed. No nutrients were added to the Os doped seawater culture solution. The jars, plus tips, were placed into an incubator with a set light/dark rhythm of 16:8, light intensity of 125 μmol photons/$m^2 \cdot s^2$ and a temperature of 11 ºC. The wet weight (WW) of the algal tips in each jar was measured every 2–3 days during the 14 day culturing period. At the same time, the seawater Os-doped culture medium was changed (5 times in total) to avoid accumulation of metabolites. The pH (~9) and salinity (~16 psu) of the Os doped seawater culture medium did not appreciably change from that of the natural seawater collected from Staithes, which is also ~9, and remained constant throughout the culture experiments. The recorded pH is higher than the normal pH range of seawater. This is probably due to the higher levels of photosynthesis relative to respiration during the day or, dissolution of carbonates from the surrounding bedrock. Following the culture experiment, each sample was oven-dried at 60 °C for 24 h and ground into a powder with an agate mortar and pestle.

2.3 Re-Os analysis

2.3.1 Macroalgae

The Re-Os abundance and isotope composition determinations for all *F. vesiculosus* samples were obtained by isotope-dilution negative ion mass spectrometry (ID-NTIMS) at the Durham Geochemistry Centre in the Laboratory for Sulphide and Source Rock Geochronology and Geochemistry. Approximately 80 to 100 mg of sample powder was utilised for the Re-Os analysis. The powdered sample was added to a Carius tube with a known amount of a mixed ^{185}Re + ^{190}Os tracer solution. To prevent any sample reaction prior to sealing, the Carius tubes were placed into an ethanol/dry ice bath and 3 mL of 11 N HCl and 6 mL of 15.5 N HNO_3 were added. After sealing, the Carius tubes were placed into an oven and heated to 220 ºC for 24 h. The Os was isolated from the acid medium using $CHCl_3$ solvent extraction, with the Os back extracted into HBr. The Os was further purified using a CrO_3-H_2SO_4 – HBr micro-distillation methodology (Birck et al., 1997; Cohen and Waters, 1996). The resultant Re-bearing acid medium was evaporated to dryness at 80 ˚C, with the Re isolated and purified using both NaOH-acetone solvent extraction and HNO_3-HCl anion chromatography (Cumming et al., 2013).

2.3.2 Seawater

The Os abundance and isotope composition of the seawater at Staithes was determined using the liquid bromine (Br_2) methodology (Gannoun and Burton, 2014) at the Laboratoire Magmas et Volcans at the Campus Universitaire des Cézeaux. In brief, ~60 g of water sample, plus a known amount of mixed (^{190}Os + ^{185}Re) tracer solution, together with 2 mL of Br_2, 2 mL of CrO_3-H_2SO_4 solution and 1.5 mL of 98% H_2SO_4 were sealed into a 120 mL Savillex vial and heated to 100˚C in an oven for 72 h. Following the spike-sample equilibrium stage, to test that excess Cr^{6+} still exists in the CrO_3-H_2SO_4 solution, a drop (~30 µl) of the aqueous phase was pipetted and added to

3% v/v H_2O_2 solution. This resulted in the CrO_3 reacting with the H_2O_2 by producing intense bubbling with a transient dense blue colour formed, thus confirming the presence of excess Cr^{6+}. Osmium was extracted from the sample into liquid Br_2. To increase the extraction yield of Os, a second extraction of Os was conducted using 1 ml of Br_2. The 1 mL of liquid Br_2 was added to the sample solution reacted for 1 hr and then removed. The extracted Br_2 was mixed with 1 ml of 9N HBr and evaporated to dryness. The Os was further purified using a CrO_3-H_2SO_4 – HBr micro-distillation. The Os extracted, Re-bearing solution was evaporated to dryness. The Re was purified as described for the macroalgae samples (NaOH-acetone solvent extraction and HNO_3-HCl anion chromatography, Cumming et al., 2013) at the laboratories at the Durham Geochemistry Centre.

2.4 Mass spectrometry

The purified Re and Os fractions were loaded onto Ni and Pt filaments, respectively and measured using NTIMS (Creaser et al., 1991; Völkening et al., 1991) on a Thermo Scientific TRITON mass spectrometer using Faraday collectors in static mode, and an electron multipler in dynamic mode, respectively. The Re and Os abundances and isotope compositions are presented with 2 sigma absolute uncertainties which include full error propagation of uncertainties in the mass spectrometer measurements, blank, spike and sample and spike weights. Full analytical blank values for the macroalgae analysis are 2.4 ± 0.04 pg for Re, 0.05 ± 0.02 pg for Os, with a $^{187}Os/^{188}Os$ composition of 0.25 ± 0.15 (1 SD, n = 3). For the seawater analysis the full analytical blank values are 10.0 ± 1.3 pg for Re, 0.043 ± 0.002 pg for Os, with a $^{187}Os/^{188}Os$ composition of 0.72 ± 0.02 (1 SD, n = 4).

To monitor the long-term reproducibility of mass spectrometer measurements Re and Os (DROsS, DTM) reference solutions were analysed. The 125 pg Re solution yields an average $^{185}Re/^{187}Re$ ratio of 0.5983 ± 0.0024 (2 SD., n = 5), which is in agreement with the published values (e.g., Cumming et al., 2013). A 50 pg DROsS solution gave an $^{187}Os/^{188}Os$ ratio of 0.16088 ± 0.0008 (2 SD., n = 5), which is in agreement with the reported value for the DROsS reference solution (Nowel et al., 2008). For the seawater Os analysis at the Laboratoire Magmas et Volcans instrument reproducibility is monitored using a 1 pg DTM Os solution, which yields an $^{187}Os/^{188}Os$ value of 0.1740 ± 0.0002 (2 SD, n = 4), which is inagreement with published values (Chen and Sharma, 2008; Gannoun and Burton, 2014).

3. Results

3.1 Re and Os abundances and isotope compositions of Staithes seawater

The Staithes seawater possesses a Re and Os abundance of 8.2 and 0.0156 ppt, respectively, with a $^{187}Re/^{188}Os$ value of 2790.6 ± 49.7 and a $^{187}Os/^{188}Os$ composition of 0.94 ± 0.04 (Table 1). The filtered seawater was doped with DROsS to create a seawater culture solution with an Os concentration 3× (~0.05 ppt), 6× (~0.1 ppt) and 200× (~3 ppt) that of seawater, which respectively have $^{187}Os/^{188}Os$ compositions of 0.38 ± 0.02, 0.29 ± 0.01, and 0.18 ± 0.01 (Table 2).

3.2 Re and Os abundances and isotope compositions within *F. vesiculosus* structures

The natural total Os abundance within all structures of *F. vesiculosus* collected during May 2014 directly from the seaward side of the Staithes harbour wall and not cultured, is between 1600 and 3700 times greater than the concentration found in seawater (Fig. 1). The Os abundance in the *F. vesiculosus* structures ranges from 16 to

38 ppt (Fig. 1; Table 1). The structure that contains the least amount of Os is the holdfast (16 ppt), with the blades possessing the highest Os abundance (38 ppt). The remaining structures (tips, stipe and vesicles) possess similar concentrations (24 and 25 ppt Os). A mixture of all the *F. vesiculosus* structures possesses ~34 ppt Os, which is reasonable if we take the value as a reference as the approximate relative proportions of each structure of *F. vesiculosus*. For example, *F. vesiculosus* is comprised of 67 % tips and blades, 30 % stipe and vesicles and 3 % holdfast (Fig. 1).

A previous study showed that the the natural Re abundance within *F. vesiculosus* varies (23 to 313 ppb) and that Re is not located in one specific structure (Racionero-Gómez et al. 2016). In agreement with this previous study, we show that the Re abundance is highly variable throughout *F. vesiculosus*, with Re abundances ranging from ~22 to 138 ppb, being between 3100 to 19700 times greater than that found in seawater (Table 1). Similar to Os, the holdfast (and stipe) possess the least amount of Re (~22 ppb). However, in contrast to Os, the tips possess the greatest enrichment of Re (~138 ppb).

The variability in Re and Os abundance means that the $^{187}Re/^{188}Os$ values for *F. vesiculosus* structures is highly variable (Table 1). The $^{187}Re/^{188}Os$ values range between ~4672 (stipe) and 30558 (tips), with the holdfast and blades possessing similar values to those of the stipe. The $^{187}Os/^{188}Os$ values for the *F. vesiculosus* structures, with the exception of the holdfast, possesses an average composition of 0.80 ± 0.03 (1 SD) that reflects a moderately radiogenic composition; this is identical, within uncertainty, to the mixture of all the structures (0.81 ± 0.04).

3.3 **Uptake of Osmium by *F. vesiculosus* culture tips**

The natural Os abundance of the tips of a specimen of *F. vesiculosus* collected in June 2015 possesses significantly less Os (7.8 ppt; Table 1) than that of the same structure from a specimen collected in May 2014 (23.5 ppt; Table 1). The same is observed for rhenium (138 ppb for May 2014 versus 47 ppb for June 2015; Table 1). This difference can be due to many different factors; location, yearly, monthly or daily changes, ocean sediment turbulence, age of the specimen and other present unknown conditions (Horta-Puga et al., 2013; Lyngby and Brix, 1982). Furthermore, to our knowledge the impacts that each specific factor produces to the flux of Re and Os to the nearshore have not been determined. Although the Re and Os abundances are different between the samples collected in May 2014 and June 2015, the $^{187}Re/^{188}Os$ compositions are similar (~30558 ± 2046 (May 2014) versus ~34794 ± 2074 (June 2015). The $^{187}Os/^{188}Os$ compositions are slightly different (0.75 ± 0.05 (May 2014) vs 0.91 ± 0.07 (June 2015); Table 2), which likley reflects their geographic positions. For example, the June 2015 samples are taken from within the Harbour at the mouth of Staithes Beck, whereas the May 2014 samples are seaward of the Harbour wall (see Section 4.2).

The tips of the *F. vesiculosus* collected in June 2015 were used for the culture experiments. For all the culture experiments the Re abundance of the tips (~67 to 79 ppb) is greater than that from specimen tips analysed directly from the ocean (~47 ppb) (Table 1). We note that the only Re present in the culture media is that present in the natural seawater (~8 pg/g; Table 1) because the Re abundance in the Os solution (DROsS) used to dope the natural seawater is negligible (e.g., 1 pg/g Os solution contains ~$7e^{-6}$ fg/g Re (Nowell et al., 2008). The Re abundance of the cultured tips shows a decrease from ~79 ppb for the 3× experiment, to ~71 ppb for the 6× experiment, and ~67 ppb for the 200× experiment (Table 1).

For osmium, the abundance increases proportionally to the amount of Os doped in the seawater (3× = ~20 ppt, 6× = ~30 ppt, 200× = ~200 ppt; Table 1; Fig. 4). Coupled with this increase in Os abundance is a trend to less radiogenic $^{187}Os/^{188}Os$ compositions (3× = 0.35 ± 0.02, 6× = 0.28 ± 0.01, 200× = 0.18 ± 0.00; Table 1; Fig. 4). Additionally, as a direct result of the overall increase of Os in the cultured tips with a relatively similar Re abundance, the $^{187}Re/^{188}Os$ composition significantly decreases (natural sample = ~32000; 3× = ~18000, 6× = ~12000, 200× = ~1600; Table 1).

4. Discussion and implications

4.1 Localization and uptake of Os within *F. vesiculosus*

Five types of cells can be distinguished in brown macroalgae: epidermal cells, primary cortical cells, secondary cortical cells, medullary cells and hyphae (Davy de Virville and Feldmann, 1961). A previous study identified that Re accumulation in *F. vesiculosus* is variable across the structural components (holdfast, blade, stipe, tips) of the macroalgae, indicating that there were some cells/structures more specialized for the uptake of Re (Racionero-Gómez et al. 2016). In the case of Os, its abundance does not signifcantly vary between structures, with the exception of the holdfast, suggesting that there is no specific cell specialization for the uptake of Os (Fig. 1; Table 1). The holdfast does not serve as the primary organ for water or nutrient uptake, instead it serves to anchor the macroalgae to the substrate. Therefore, lower Os abundances in the holdfast are expected. Moreover, it is suggested that Re could be biologically influenced (Racionero-Gómez et al. 2016), with uptake controlled by the growing season, as observed for zinc, lead and copper (Riget et al., 1995, Fuge and James, 1973). As such, this may also be the case for Os, however we cannot conclusively state that Os uptake is biologically controlled, because our samples were collected principally during the same

growing season. Although, this may explain, in part, the varaibility in Re and Os abundance between the May 2014 and June 2015 samples as noted above. Nevertheless, the uptake of Os by *F. vesiculosus* is similar to that of Re, in the sense that, it is currently known to have no biological role. Further, the difference in Os isotopic composition between each structure cannot be considered significant given that all values overlap within uncertainty, with the exception of the holdfast (see Table 1).

The measured Os abundance in the cultured *F. vesiculosus* tips show a positive correlation with the concentration of Os doped seawater (see Tables 1, 2; Fig. 4). The culture experiment with the highest Os concentration (200× (3 ppt Os) seawater), resulted in tips possessing an Os abundance of ~194 ppt, which is ~25 times higher than the background concentration of Os in the specimens collected (Table 1).

Using the $^{187}Os/^{188}Os$ composition of the Staithes seawater (0.94 ± 0.04), together with the background Os abundance in the tips of the June 2015 collection (~8 ppt; Table 1), with the concentration of the doped seawater and cultured tips and their $^{187}Os/^{188}Os$ composition, we observe that the percentage of Os that has been transferred from seawater to the algae is about 17 % (Table 2).

Coincident with the increase in Os abundance within the culture experiments is the decrease in Re (Table 1), indicating possible competition between similar cell binding sites or uptake pathways between Re and Os, both forming oxoanions in seawater. However, the uptake pathways and binding sites of Re have not yet been identified, thus it is currently not known where Os accumulates in *F. vesiculosus*.

4.2 Implications of the $^{187}Os/^{188}Os$ isotope composition of *F. vesiculosus*

The $^{187}Os/^{188}Os$ composition of *F. vesiculosus* in a natural setting from the harbour at Staithes is 0.91 ± 0.07 (Table 1; Fig. 4) based on results from specimens

collected in June 2015, which is within uncertainty to that of the seawater from the same location (0.94 ± 0.04) (Table 1). The agreement of the *F. vesiculosus* and seawater $^{187}Os/^{188}Os$ compositions would imply that macroalgae records the $^{187}Os/^{188}Os$ composition of the watermass it is living in. This is further supported by the culture experiments. For each culture experiment the measured $^{187}Os/^{188}Os$ composition of the tips coincides with the $^{187}Os/^{188}Os$ composition of doped seawater (Table 2; Fig. 4). This indicates that the $^{187}Os/^{188}Os$ composition of seaweed reflects the media in which it grows, and thus directly supports the use of *F. vesiculosus* (and macroalgae) as a biological proxy for the $^{187}Os/^{188}Os$ composition in seawater (Rooney et al, 2016). For example, the $^{187}Os/^{188}Os$ composition for three floating macroalgae (*Sargassum fluitans* and *S. natans*) collected from three different locations ~300 miles offshore in the Gulf of Mexico (1.05 ± 0.01; Rooney et al, 2016) are coincident with that of the present day open oceanic $^{187}Os/^{188}Os$ value of 1.06 (1.04 for the North Atlantic and Central Pacific; 1.06 for the Eastern Pacific and Indian Ocean) determined from direct analyses of seawater and of hydrogenetic Fe-Mn crusts (see Peucker-Ehrenbrink and Ravizza, 2000 and references therein; Gannoun and Burton, 2014 and references therein). In contrast, macroalgae from the coast of the Disko Bugt and Uummannaq regions of the west coast of Greenland show deviations from the $^{187}Os/^{188}Os$ composition of the open ocean (between 0.9 and 1.9) which directly relate to Os flux (abundance and isotope compositon) into the coastal region (Rooney et al., 2016). The latter together with the slightly lower and variable $^{187}Os/^{188}Os$ composition (~0.91 (June 2015 Staithes harbour) vs ~0.81 (Staithes east of the harbour wall); Table 1) of the macroalgae from Staithes in comparison to that of the open sea may suggest that the Os isotope composition of macroalgae is strongly controlled by its proximity to the coast, riverine input and regional variations in the Os flux (i.e., abundance and isotope composition) into the

ocean, as also shown along the transects of estuaries (e.g., Levasseur et al., 2000; Martin et al., 2001; Sharma et al., 2007). For example, the Fly River Estuary reflects the input of unradiogenic Os and shows an increasing $^{187}Os/^{188}Os$ composition oceanward from 0.61 to 0.91 (Martin et al., 2001). In contrast, the Lena River Estuary and the Godavari Delta reflects the input of radiogenic Os, with the $^{187}Os/^{188}Os$ value decreasing oceanward from 1.55 to 1.13, and 1.30 to 0.90, respectively (Levasseur et al., 2000; Sharma et al., 2007). Moreover, surface seawater has a distinctly lower $^{187}Os/^{188}Os$ than the deep ocean (Chen et al., 2009; Gannoun and Burton, 2014). Therefore, macroalgae from distinct oceanic settings (e.g., coastal, estuarine versus open ocean) provides the ability to record the $^{187}Os/^{188}Os$ composition of seawater in addition to direct seawater and sediment analysis to further access the factors (e.g., geological and anthroprogenic) controlling the $^{187}Os/^{188}Os$ composition of seawater.

4.3 Implications of the $^{187}Re/^{188}Os$ isotope composition of *F. vesiculosus*

In addition to the $^{187}Os/^{188}Os$ composition of macroalage, the $^{187}Re/^{188}Os$ values of macroalgae (this study; Rooney et al., 2016) may provide insight into the variability of the $^{187}Re/^{188}Os$ in sediments as organic matter. The $^{187}Re/^{188}Os$ values for staithes seawater (2790.6 ± 49.7) falls somewhere between open ocean (4270; Anbar et al., 1992; Coloder et al., 1993; Sharma et al., 1997; Levassuer et al., 1998; Woodhouse et al., 1999; Peucker-Ehrenbrik and Ravizza, 2000) and riverine (227; Coloder et al., 1993b; Sharma and Wasserburg, 1997; Levassuer et al., 1999; Peucker-Ehrenbrik and Ravizza, 2000) estimates, as expected for estuarine conditions. However, the $^{187}Re/^{188}Os$ values of macroalgae from this study (34794.1 ± 2074.4) are far higher suggesting that the $^{187}Re/^{188}Os$ ratios in macoralgae are not proportional to the seawater

384 in which they live, but controlled by the uptake mechanism(s) of macroalgae that are
385 currently unknown.

386 To date, it is known that the Re abundance in macroalgae can be highly variable
387 (sub ppb to tens of ppb; Scadden, 1969; Yang, 1991; Mas et al., 2005; Prouty et al.,
388 2014; Racionero-Gómez et al., 2016; Rooney et al., 2016). For osmium, the results thus
389 far also indicate that the Os abundance in macroalgae can also be highly variable (this
390 study; Rooney et al, 2016). Further, in addition to macroalgae that are components of
391 sediment organic matter, microorganisms can also accummulate Re (Prouty et al., 2014;
392 Mashkani et al., 2009; Ghazvini and Mashkani, 2009), although to date, no data exists
393 for osmium. Given the variability of Re and Os uptake by macroalgae, the $^{187}Re/^{188}Os$
394 composition of macroalgae is seen to range from ~10 to ~35,000 (this study; Rooney et
395 al., 2016). Metabolically inactive (i.e dead) macroalgae (*F. vesiculosus*) does not
396 appreciably accummulate rhenium (Racionero-Gómez et al., 2016). If Os in
397 metabolically inactive macroalgae and/or microogranisms is not accumulated or
398 released, then the Re and Os abundance, and isotope composition could be dominantly
399 controlled by the abundance, variability, and the structural type of the organisms
400 preserved in a sediment as organic matter rather than purely sequestration at the
401 sediment-water interface (Yamashita et al., 2007 and references therein). As such,
402 organic matter and organic type, in addition to the depositional setting conditions
403 (Yamashita et al., 2007; Georgiev et al., 2011), maybe important factors in controlling
404 Re/Os fractionation observed in organic-rich sediments (Cumming et al., 2012; Harris et
405 al., 2012).

406 A further implication of the uptake of Re and Os by organisms could be its
407 effect on the Re-Os organic-rich sedimentary geochronology. In addition to the Re-Os
408 isotope system remaining undisturbed and for the samples to possess a range in

409 $^{187}Re/^{188}Os$ values, the stratigraphic interval must possess similar initial $^{187}Os/^{188}Os$
410 values to provide reliable (accurate and precise) dates of sediment deposition (Cohen et
411 al., 1999; Selby and Creaser, 2003). As such the heterogenous mixing of organisms with
412 variable $^{187}Os/^{188}Os$ compositions in a sedimentary rock could hamper the ability to
413 yield precise Re-Os dates. This could be particularly problematic in nearshore
414 depositional settings of organic-rich sediments. For example, in a estuarine or deltaic
415 sedimentary system the $^{187}Os/^{188}Os$ composition is variable along its transect (Levasseur
416 et al., 2000; Martin et al., 2001; Sharma et al., 2007). Further, macroalgae from
417 Greenland within Disko Bay show a 0.05 difference in their $^{187}Os/^{188}Os$ composition
418 (Rooney et al., 2016). As such, organisms along the transect may also have variable
419 $^{187}Os/^{188}Os$ compositions. Therefore any heterogeneous mixing of organisms that are
420 preseved as organic matter within a sediment with different $^{187}Os/^{188}Os$ compositions
421 could impact on the precision of Re-Os organic-rich sedimentary geochronology.
422
423 **5. Conclusions**
424 Culture experiments indicate that macroalgae acquires the $^{187}Os/^{188}Os$
425 composition of the media in which it grows. As a result this suggests that macroalgae
426 are a viable biological proxy to determine the $^{187}Os/^{188}Os$ composition of seawater in
427 various oceanographic settings. Specifically in coastal settings the $^{187}Os/^{188}Os$
428 composition of macroalgae could be used to assess the $^{187}Os/^{188}Os$ composition of
429 continental input in to the ocean.
430
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588 **Figures and captions**
589
590 Figure 1. Photo exhibiting the key structures of *F. vesiculosus*. Also shown are the Re
591 and Os abundances, and Re-Os isotope compositions (Data including uncertainties are
592 given in Table 1).
593
594 Figure 2. *F. vesiculosus* sample locations for May 2014 and June 2015.
595
596 Figure 3. Representation of culture growth set-up of non-reproductive *F. vesiculosus*
597 thallus tips. (**A**) Two meshes were put inside each jar generating three levels that each
598 hold three non-fertile tips each. (**B**) Photo of the culture jar used.
599
600 Figure 4. Osmium (ppt) accumulation (circles) and $^{187}Os/^{188}Os$ compositions (squares)
601 in *F. vesiculosus* under different Os seawater culture media concentrations. The open
602 symbols are for *F. vesiculosus* collected June 2015. See Tables 1 and 2 for data.
603
604

Table

Table 1. Rhenium (ppb), Osmium (ppt) and Re-Os isotope compositions in *F. vesiculosus* structures and culture experiment.

Sample	Weight (g)	Re (ppb)	Os (ppt)	$^{187}Re/^{188}Os$	$^{187}Os/^{188}Os$
May 2014 collection					
Tips	0,201	138.0 ± 0.7	23.5 ± 0.7	30558.8 ± 2046.6	0.75 ± 0.05
Blades	0,200	56.8 ± 0.3	37.6 ± 0.7	7902.1 ± 336.9	0.78 ± 0.04
Stipe	0,200	22.5 ± 0.2	25.2 ± 0.7	4672.6 ± 299.8	0.81 ± 0.05
Holdfast	0,200	21.6 ± 0.2	16.0 ± 0.7	7223.4 ± 736.2	0.95 ± 0.10
Vesicles	0,200	59.0 ± 0.4	24.8 ± 0.7	12476.6 ± 805.9	0.80 ± 0.05
Mix of structures	0,204	64.0 ± 0.7	33.8 ± 0.7	9930.3 ± 469.9	0.81 ± 0.04
June 2015 collection					
Tips	0,101	47.4 ± 0.1	7.8 ± 0.4	34794.1 ± 2074.4	0.91 ± 0.07
Culture experiment					
1- 3x seawater[1]	0,102	79.3 ± 0.2	21.2 ± 0.4	18585.9 ± 866.6	0.35 ± 0.02
2- 3x seawater[1]	0,101	77.7 ± 0.2	20.5 ± 0.1	18819.6 ± 757.5	0.34 ± 0.01
1- 6x seawater[1]	0,102	71.3 ± 0.2	28.6 ± 0.5	12235.8 ± 421.2	0.28 ± 0.01
2- 6x seawater[1]	0,102	71.1 ± 0.2	32.7 ± 0.5	10696.6 ± 323.4	0.28 ± 0.01
1- 200x seawater[1]	0,081	67.1 ± 0.2	201.6 ± 0.8	1615.0 ± 12.7	0.18 ± 0.00
2- 200x seawater[1]	0,081	66.8 ± 0.2	194.3 ± 0.8	1668.6 ± 13.4	0.18 ± 0.00
Staithes seawater					
seawater[2]	64,5	8.20 ± 0.08	15.7 ± 0.2	2790.6 ± 49.7	0.94 ± 0.04

[1]Culture experiment uses tips from specimens collected in June 2015

[2]seawater Re concentrations in ppt; Os concentrations given in ppq

All uncertainties are quoted at the 2s level

The Re-Os abundances are based on the dry mass of the seaweed

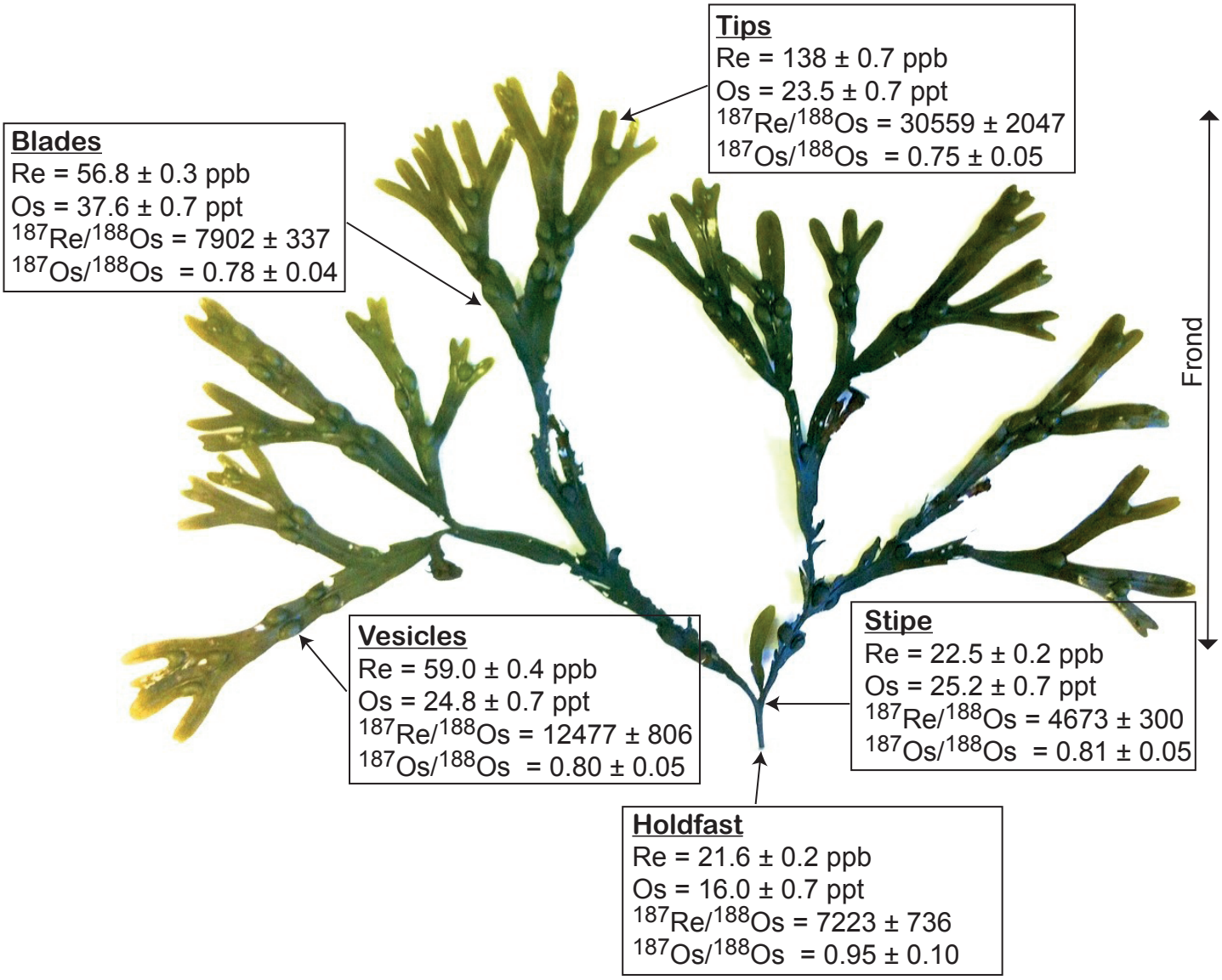
Table

Table 2. Osmium (ppt) and 187Os/188Os compositions in the culture media and in *F. vesiculosus.*

Sample	Seawater [Os] (ppt)	$^{187}Os/^{188}Os$ of seawater culture media	Measured $^{187}Os/^{188}Os$ of seaweed after culture growth	% of Os transferred from seawater culture media into the seaweed
Natural seawater[1]	0,0156	0.94 ± 0.04		
3x seawater	0,05	0.38 ± 0.02	0.35 ± 0.02	17,4
6x seawater	0,1	0.29 ± 0.01	0.28 ± 0.01	16,8
200x seawater	3	0.18 ± 0.01	0.18 ± 0.00	16,9

[1]Measured seawater from Staithes - see Table 1

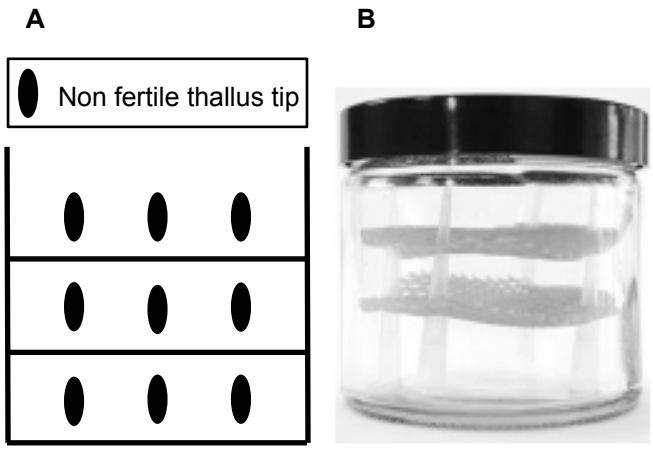
Figure


Tips
Re = 138 ± 0.7 ppb
Os = 23.5 ± 0.7 ppt
187Re/188Os = 30559 ± 2047
187Os/188Os = 0.75 ± 0.05
Blades
Re = 56.8 ± 0.3 ppb
Os = 37.6 ± 0.7 ppt
187Re/188Os = 7902 ± 337
187Os/188Os = 0.78 ± 0.04
Frond
Vesicles
Re = 59.0 ± 0.4 ppb
Os = 24.8 ± 0.7 ppt
187Re/188Os = 12477 ± 806
187Os/188Os = 0.80 ± 0.05
Stipe
Re = 22.5 ± 0.2 ppb
Os = 25.2 ± 0.7 ppt
187Re/188Os = 4673 ± 300
187Os/188Os = 0.81 ± 0.05
Holdfast
Re = 21.6 ± 0.2 ppb
Os = 16.0 ± 0.7 ppt
187Re/188Os = 7223 ± 736
187Os/188Os = 0.95 ± 0.10

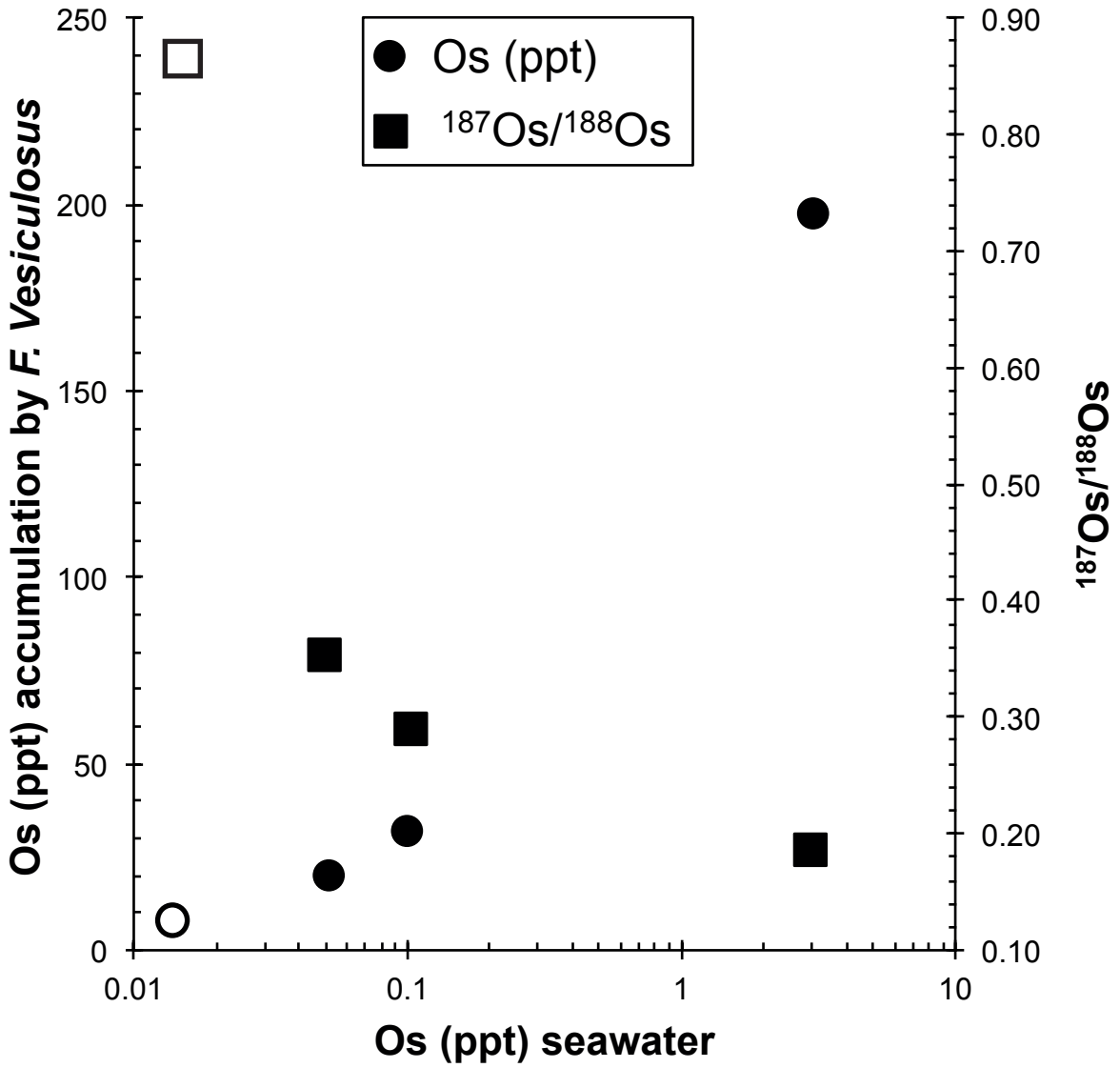
Figure


N
Harbour Walls
May 2014
collection
June 2015
collection
50 m

Figure



Figure


Os (ppt)
187Os/188Os
Os (ppt) accumulation by F. Vesiculosus
187Os/188Os
Os (ppt) seawater
250
200
150
100
50
0
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.01
0.1
1
10